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Infrared multiple photon dissociation (IRMPD) spectra in the 9.2 - 10.8 μm wavelength range have been obtained for the protonated molecular ion of bis(methoxydiethyl) ether (diglyme), and the molecular ions of 3-bromopropene and gallium hexafluoroacetylacetonate, using one and two lasers. Use of a low-power tunable CO_2 laser and a modified White-type multipass FTICR cell has helped to overcome some limitations of this technique, including a limited tuning range and/or low output power in one-laser experiments. Comparisons between the ion spectra and those of the corresponding neutral species are made.

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Infrared Multiple Photon Dissociation Spectra of Gaseous Ions

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Abstract

Infrared multiple photon dissociation (IRMPD) spectra in the 9.2 - 10.8 μm wavelength range have been obtained for the protonated molecular ion of bis(methoxy diethyl) ether (diglyme), the positive molecular ion of 3-bromopropene and the negative molecular ion of gallium hexafluoroacetylacetonate, using one and two lasers. Use of a low-power tunable CO_2 laser, a second, more powerful, CO_2 laser and a modified White-type multipass FTICR cell has helped to overcome some limitations of this technique, including a limited tuning range and/or low output power in one-laser experiments. Comparisons between the ion spectra and those of the corresponding neutral species are made.

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Introduction

Spectroscopic studies of molecular ions have become a challenging and an interesting area of study in recent years.^{1,2} Unlike neutral molecules and ions in solution or in the solid state, for which IR, UV-Vis and NMR spectroscopies give useful structural information, there is no general direct method to obtain structural information for gaseous ions. Although infrared spectroscopy has been used on very small ions,^{3,4} its application has been limited. This limitation arises primarily from the difficulty of obtaining a high enough density of ions of a known mass in a small volume to yield a measurable absorbance, thus leading to reliable spectra. One is most often forced, then, to utilize an indirect method, such as ion photodissociation, to obtain spectra and structural information for gaseous ions.

In ion photodissociation, an ion absorbs one or more photons until it gains sufficient energy to dissociate into fragments. The disappearance of parent ion or the appearance of the fragment ions as a function of irradiation wavelength can then lead to a photodissociation spectrum of the parent ion under favorable conditions.⁵ This approach has exhibited reliable results for interpretation of energy levels, dissociation thresholds, and structures of gaseous ions, when they are subjected to UV-visible irradiation, quite often in Fourier transform ion cyclotron resonance (FTICR) mass spectrometers.⁶⁻⁹

The technique of infrared multiple photon dissociation (IRMPD) of ions has been used in isolated instances by several researchers¹⁰⁻¹⁵ to obtain spectra of gaseous ions in order to assist in determining ion structure. Y.T. Lee et. al. demonstrated the feasibility of IRMPD of molecules in molecular beams¹⁶ and obtained structural information as well as thermal decomposition data for polyatomic molecules. However, due to both the limited tunability of standard ir laser sources (CO₂, CO, NO), and partly to the low power of these lasers, there has been no systematic attempt to use IRMPD to obtain gaseous ion spectra and structural information.

Our laboratory has been heavily involved¹⁷⁻²² in coupling UV-visible and both continuous wave (cw) and pulsed CO₂ lasers to FTICR mass spectrometers for several years. As a result of these investigations structural information about isomeric ions^{23,24} and some crude spectra for diol ions²⁵ have been obtained, but the above mentioned limitations precluded acquisition of high quality IRMPD spectra. However, a novel two-laser approach developed in our laboratory^{26,27} has demonstrated that reproducible spectroscopic data for gaseous ions can be obtained, and this technique promises to overcome many of the limitations imposed by the use of CO₂ and other lasers.

An ion with a sufficiently high density of vibrational and rotational levels is excited to the "quasicontinuum" by resonant multiphoton absorption from a low-power tunable pulsed CO₂ laser. In the quasicontinuum the ion can readily absorb additional photons regardless of their energy. These additional photons, provided by a more powerful cw CO₂ laser, impart sufficient internal energy to the ion to dissociate it into fragments, which are observed using standard FTICR detection techniques.

The applicability of our recently developed method for obtaining spectra of gaseous ions, using a low power tunable pulsed CO₂ laser for probing the resonant absorption spectrum and a more powerful non-resonant cw CO₂ laser to complete the dissociation,

is demonstrated in the work reported here. In particular, one and two laser spectra for the protonated bis(methoxy diethyl) ether (diglyme) cation, the 3-bromopropene (allyl bromide) cation, and the gallium hexafluoroacetylacetonate anion ($[\text{Ga}(\text{hfac})_3]^-$) have been obtained.

Experimental Section

All IRMPD experiments were performed on a home-built FTICR mass spectrometer, equipped with a 2T superconducting magnet, and controlled by a Nicolet²⁸ FTMS 1000 data station. The 15.2 cm i.d. vacuum chamber was pumped by two diffusion pumps with 300 and 700 L s^{-1} pumping speeds, respectively. The background pressure was maintained below 2×10^{-9} Torr and samples were leaked in through a precision leak valve up to a pressure of 5.5×10^{-8} Torr.²⁹ The mass spectrometer was operated in the "broad-band" mode in which ions with frequencies of 2.667 MHz to 10 kHz, corresponding to a mass range of 12 to 2000 Da, were excited. Generally, for each spectrum 16,384 data points were acquired by signal averaging 50-100 ion transient response signals. The time domain signals were then apodized³⁰ and zero-filled once before being subjected to Fourier transformation.

To enhance photodissociation effects the FTICR analyzer cell used in these experiments was modified to increase the irradiation path length by a multipass arrangement first described by White.³¹ This White-type ICR cell was first demonstrated in our laboratory for IRMPD experiments using a single laser, and was shown to enhance dramatically ion photodissociation effects. In the present study the White-type cell was used to obtain spectra for both one and two laser experiments.

The cell dimensions are 2.5 cm, 2.5 cm, and 6.5 cm along the x, y, and z (magnetic field) axes, respectively. Three spherical, concave, well-polished brass mirrors are incorporated as the receive plates of the ICR cell, and the excite plates have been replaced with stainless steel screens (see Figure 4 of reference 26 for more details). A turning mirror is attached to one end of one receive plate to reflect the resonant laser light into the cell, and thus to begin the multipass reflection process. In two-laser experiments the non-resonant cw laser enters via one of the trap plates, which was modified by addition of a 1.75 cm diameter hole covered with a coarse stainless steel mesh.

Single-laser experiments were performed using an Apollo Model 570 cw CO_2 laser,³² which can be tuned over a wavelength range of 9.0 - 11.3 μm . The laser was gated on for variable length irradiation periods (ranging from 50 to 500 ms) by the FTICR data station at a constant energy of 1J pulse^{-1} . Two-laser experiments were performed with a Lumonics Model TE 860 CO_2 laser³³ as the resonant probe laser and the Apollo laser as the non-resonant pump laser. The probe laser is line tunable over a wavelength range of 9.10-10.92 μm , and its energy was kept constant at $100 \pm 15\text{ mJ pulse}^{-1}$. Triggering of this laser was also controlled by the FTICR data station. All energies reported here were measured in front of the laser head (the pulsed laser has a rectangular beam profile of 2 cm x 2.75 cm at this point), and we estimate ca. 50% of this beam entered the ICR cell. For two-laser experiments the pump laser was operated at a fixed wavelength of 10.58 μm and a constant energy of 1J pulse^{-1} (beam diameter is 0.8 cm).

The laser beams enter the vacuum chamber through two ZnSe windows mounted on a three window flange. As shown in Figure 1, the pulsed CO₂ (probe) laser beam is reflected by the turning mirror into the cell, and subsequently reflected from the spherical mirrors to create multipasses. The cw CO₂ (pump) laser enters the vacuum chamber through a second window, passes into the cell through one of the trapping plates, and reflects from the other trapping plate, thus giving a double pass inside the cell.

Ions were formed by electron ionization. The electron beam voltage was varied from 10-30 volts for the cations and the anion was formed by electron attachment using a low energy electron beam (0.5 V). The molecular ion of interest was isolated by ejecting all other ions from the cell.³⁴ Ions were then allowed to undergo several collisions with the neutrals at a pressure of 5.5×10^{-8} Torr for approximately 1s. No difference in photodissociation was observed as this collision time was varied over a (limited) range of 0.75 to 1.5 s. Subsequent to this "cooling period" the probe laser was fired and another series of ion ejections was used to remove any unwanted adducts and fragments formed by the probe laser. These ejections were carried out with a minimum time delay (<30ms) before the pump laser irradiation period. Then the pump laser was gated on for 30ms. All ions present after this time were excited and detected, and the extent of photodissociation was obtained by measuring the intensities of the parent and fragment ions, as given by their mass spectral peak areas. The pulse sequences for both one-laser and two-laser (probe-pump) approaches are depicted in Figure 2.

A positive trapping potential of 3 to 4 V was used for diglyme and 3-bromopropene cations, and a potential of -2 to -3 V was used for [Ga(hfac)₃]⁻. These higher than usual trapping potentials are necessary when using the White-type cell, because of the distortion of the electric field lines in the analyzer cell due to the curved receive plates.

To obtain the gas phase spectra of neutral allyl bromide and diglyme a 10 cm path length quartz cell with KBr windows was used in a Nicolet 7199 FTIR spectrometer. The cell was filled to a pressure of 0.45 Torr for each compound. The [Ga(hfac)₃] spectrum was obtained in the solid state (KBr pellet) with a Perkin Elmer 1600 FTIR spectrometer.

All samples were obtained from commercial sources. Purity was confirmed by broadband mass spectra and the samples were used without further purification.

Results

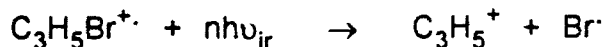
The first series of experiments was performed using the White-type multipass FTICR cell and one tunable higher power cw laser. The total energy per pulse was kept constant as the laser was tuned to various photodissociation wavelengths. The percent photodissociation (calculated by dividing the relative intensities of the photofragments by the relative intensities of all ions detected) as a function of laser wavelength was obtained for each of the three compounds.

When the cw laser was tuned through the wavelength range 10.49 -10.71 μm (953 - 934 cm^{-1}), the positive ion C₆H₁₅O₃⁺ (protonated diglyme cation, m/z=135), underwent IRMPD to form two fragment ions at m/z =103 (C₅H₁₁O₂⁺) and m/z=59 (C₃H₇O⁺) according to the reactions:



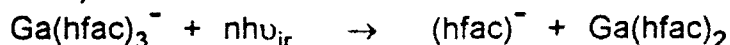
The photodissociation spectrum obtained is shown in Figure 3(a).

A limited wavelength IRMPD study of the 3-bromopropene positive ion has been previously reported.³⁵ The ion undergoes IRMPD yielding exclusively $C_3H_5^+$ via loss of Br^- .



The single laser IRMPD spectrum obtained for this ion is shown in Figure 3(b) for CO_2 laser wavelengths from 10.18 to 10.70 μm (982 - 934 cm^{-1}).

The $Ga(hfac)_3$ anion ($m/z=691$) was formed by low energy electron attachment. When the CO_2 laser was tuned from 9.49 to 9.62 μm (1054 - 1039 cm^{-1}) the negative ion photodissociated by losing a negatively charged ligand (hexafluoroacetylacetonate, $m/z=207$).



The photodissociation spectrum obtained is shown in Figure 3(c).

In a second series of experiments, useful two laser photodissociation spectra were obtained using the same compounds as discussed above and the probe-pump technique. Figures 4 (a), (b), and (c) present the spectra of protonated diglyme, allyl bromide and gallium hexafluoroacetylacetonate ions, respectively.

For comparison, gas phase neutral IR spectra were obtained for all three compounds used in this study. They are shown in Figures 5 (a), (b), and (c). Table I summarizes IR peak frequencies for the three ions obtained from Figs. 3 and 4 (one- and two-laser experiments gave identical results) and also includes the corresponding neutral IR peak frequencies for the relevant vibrations from Fig. 5. The observed peak frequency shifts are also given.

Discussion

Previous studies of IRMPD behavior of the hexafluoropropene cation ($C_3F_6^+$)²⁶ demonstrated that a relatively low-power probe laser source (ca. 100 mJ pulse⁻¹), while incapable of inducing photodissociation by itself, could be used in conjunction with a higher power pump laser source to obtain photodissociation spectra in a similar manner to higher power single laser experiments. Similar results were found for the two-laser studies of the three compounds examined here.

The one- and two-laser spectra are quite similar, as both approaches use the cw CO_2 laser to up-pump the population in high, dense vibrational states to the quasicontinuum. This similarity does lend credence to the assertion that resonant photon absorption is the "bottleneck" to dissociation in each process. Examination of Figures 3 and 4 reveals that the maximum percent photodissociation obtained for the one laser experiments was greater than that for the two laser spectra. This difference in dissociation can be explained by the much lower energy per pulse of the resonant laser in the two- versus one-laser experiments. As mentioned in the experimental section, the one-laser experiments were carried out at 1 J total irradiation energy, whereas for the two-laser experiments the resonant laser energy was kept constant at 100 mJ pulse⁻¹. The maximum per cent photodissociation was decreased only by a factor of 3-5 for all two-laser experiments performed, even though there was a tenfold decrease in total

energy per pulse of the resonant laser.

Because of their molecular complexity, the protonated diglyme and $\text{Ga}(\text{hfac})_3$ anion are expected to be near or beyond the "large molecule limit"¹¹: given their thermal energies and large numbers of internal degrees of freedom, they are either in the vibrational quasicontinuum or reach it after the absorption of only one CO_2 laser photon. The allyl bromide cation, however, is expected to be much closer to the "small molecule limit,"¹¹ where several infrared photons must be absorbed before it reaches the quasicontinuum.

In future experiments, the pulsed CO_2 probe laser will be replaced by an IR extension package,³⁶ which generates wavelengths in the 1.54 - 4.5 μm region by difference frequency mixing of the output of a Nd:YAG pumped dye laser and the residual 1.06 μm Nd:YAG laser beam. Use of this probe laser should permit us to obtain infrared spectra of gaseous ions which contain O-H, N-H, and C-H stretching modes. Even though the energies per pulse from the IR extension package are low, satisfactory results should be obtained given two-laser photodissociation produced in the present work.

Comparison of IRMPD and neutral IR spectra must be done with care due to limitations in resolution and spectral coverage in the IRMPD experiments. The gaseous ions undergo at most one collision during the photodissociation period, and thus their spectra will not be collisionally broadened, as the gas phase neutral spectra are expected to be. Thus, ions of low molecular complexity will exhibit sharp peaks with a spacing which is, in general, not the same as that between the CO_2 laser lines used for irradiation. Peaks seen in the IRMPD spectra will be the result of coincidences between the sharp absorption bands and the sharp laser lines. Only for ions of high molecular complexity, which are expected to be in the quasi-continuum even for absorption of the first photon, might a broader absorption spectrum be expected. For these, the IRMPD spectra should more closely approach the ion (and corresponding neutral) spectra, although the lack of sharp spectral features will reduce the chance of obtaining significant structural information about the ions.

Since the IR spectrum of neutral diglyme (Fig. 5a) shows a number of features in the 950 - 1250 cm^{-1} wavenumber region, exact assignment of the IRMPD peak is difficult. We have tentatively related the ion peak to the somewhat structured neutral peak between 960 and 1050 cm^{-1} , rather than to any of the stronger bands between 1100 and 1250 cm^{-1} , primarily because the absorbance of the former band is similar to that of the allyl bromide neutral band (Fig. 5b) and the IRMPD spectra of the corresponding ions show almost the same extent of photodissociation. It is not possible to assign the ion peak unambiguously to specific lines in the P or R branches of the neutral, or to the sharp Q branch of approximately the same width.

A possible explanation for the relatively small shift in frequency between the diglyme neutral and protonated ion is that while formation of protonated diglyme involves addition of H^+ onto an O atom [$\text{C}-\text{O}^+(\text{H})-\text{C}$], this results in only a small change in the nature of the bonding orbitals controlling the force constant for the C-O-C stretch. Similarity in 3-bromopropene ion and neutral spectra can be attributed to the fact that the electron removed upon formation of the positive ion is in a bromine non-bonding orbital and thus there is negligible change in the bonding orbitals controlling the force constant

for the C-Br stretch upon ionization.

In contrast, the IRMPD spectrum of $\text{Ga}(\text{hfac})_3^-$ shows a much larger shift when compared to the IR spectrum of its neutral precursor. The IR spectra of fluorine-substituted compounds have C-F stretching absorptions in the $1350\text{-}1000\text{ cm}^{-1}$ range, with the exact position depending on the nature and the degree of fluorination.³⁷ As the complexity of the molecule increases the accurate assignment of any one peak to a particular normal mode becomes complicated. This is partly due to Fermi resonance³⁸ and partly due to bonds having similar vibrational frequencies.

Assignment of the observed C-F stretching frequencies in the $\text{Ga}(\text{hfac})_3^-$ anion spectrum (Fig. 4c) and the neutral IR spectrum (Fig. 5c) is made by comparison with previous studies³⁹⁻⁴¹ in Table II. For CF_3 , CF_3^+ , and C_2F_6 the degenerate C-F stretching mode has a higher frequency than the nondegenerate C-F stretching mode. We assume a similar assignment for $\text{Ga}(\text{hfac})_3^-$ with the degenerate C-F stretching mode assigned a higher frequency (ca. 1240 cm^{-1}) and the nondegenerate C-F stretching frequency assigned a lower frequency (1151 cm^{-1}). Two peaks are observed for the degenerate C-F stretching mode at 1217 cm^{-1} and 1262 cm^{-1} ; presumably the splitting is due to Fermi resonance involving either a combination or an overtone band of one or two of the peaks observed at lower frequencies in Fig. 5c.

Shin and Beauchamp have obtained IRMPD spectra of some organometallic compounds containing CF_3 ligands.^{13,42} Two peaks in the $\text{CF}_3\text{Mn}(\text{CO})_5$ neutral spectrum were attributed to C-F stretching modes of A_1 and E symmetry respectively, and shifts to lower frequency of each peak were seen in both $\text{CF}_3\text{Mn}(\text{CO})_3(\text{NO})^-$ and $\text{CF}_3\text{Mn}(\text{CO})_4^-$. Explanation for these shifts involved increase of the electron density in the carbon σ -donor orbital of the CF_3 group in the anionic species. Also, the spectra apparently show that the frequency of the degenerate C-F stretching mode is more sensitive to changes in the net charge of the molecule and ligand substituents, leading to a larger frequency shift when compared with that of the nondegenerate C-F stretching mode (cf. the results for CF_3^+ vs. CF_3^- in Table II).

We have assumed a similar trend in A and E mode shifts in assigning the peak(s) observed for $[\text{Ga}(\text{hfac})_3]^-$ in Fig. 4c to the asymmetric C-F stretch. The electron added in formation of the anion occupies an orbital with strong anti-bonding character localized on one or more of the hfac ligands. This will definitely lead to a lowering of the C-F stretching frequency in the anion when compared to the neutral. Given the relatively narrow wavelength range spanned by Fig. 4c, it is not possible to assign unambiguously the peaks seen there. Both the symmetric and asymmetric C-F stretching modes may have been reduced by ca. 100 cm^{-1} and 200 cm^{-1} , respectively, leading to the two peaks seen in the spectrum. Or, more likely, the spectrum may be due to a single peak split by a Fermi resonance interaction of either the symmetric or the asymmetric stretching mode with one (overtone) or two (combination) modes of the correct symmetry of lower frequency which cannot be observed given the limited wavelength range of the CO_2 laser.

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Table I. Gaseous ion vibrational frequencies from one- and two-laser studies, frequencies of the corresponding gas phase neutrals, and the ion-neutral peak shifts.

Molecule	Vibrational mode	Peak frequencies (cm ⁻¹)		Shift (cm ⁻¹)
		one- and two-laser	neutral	
Diglyme	C-O-C	940.5	1030	ca.90, ^a
Allyl-bromide	C-Br	944.2	920	ca.24
		951.2	930	ca.21
		972	977	
		975.9	981	ca.5
		979.7	985	
Ga(hfac) ₃	C-F	1043.2	1151	^a
		1052.1	1240	^a

^a Neutral-ion peak shifts cannot be determined since the ion peaks cannot be assigned unambiguously. See text.

Table II. The C-F stretching frequencies of A and E modes used in assigning peak frequencies for the Ga(hfac)₃ neutral and the anion.

Molecule	A ₁ (cm ⁻¹)	E(cm ⁻¹)	Ref. #
CF ₃ [·]	1084	1252	39,40
CF ₃ ⁺	1125	1667	40
C ₂ F ₆	1116	1250	41
Ga(hfac) ₃	1151	1240	
Ga(hfac) ₃ ⁻	^a	^a	

^a Cannot be assigned unambiguously, see explanation in text.

Figure Captions

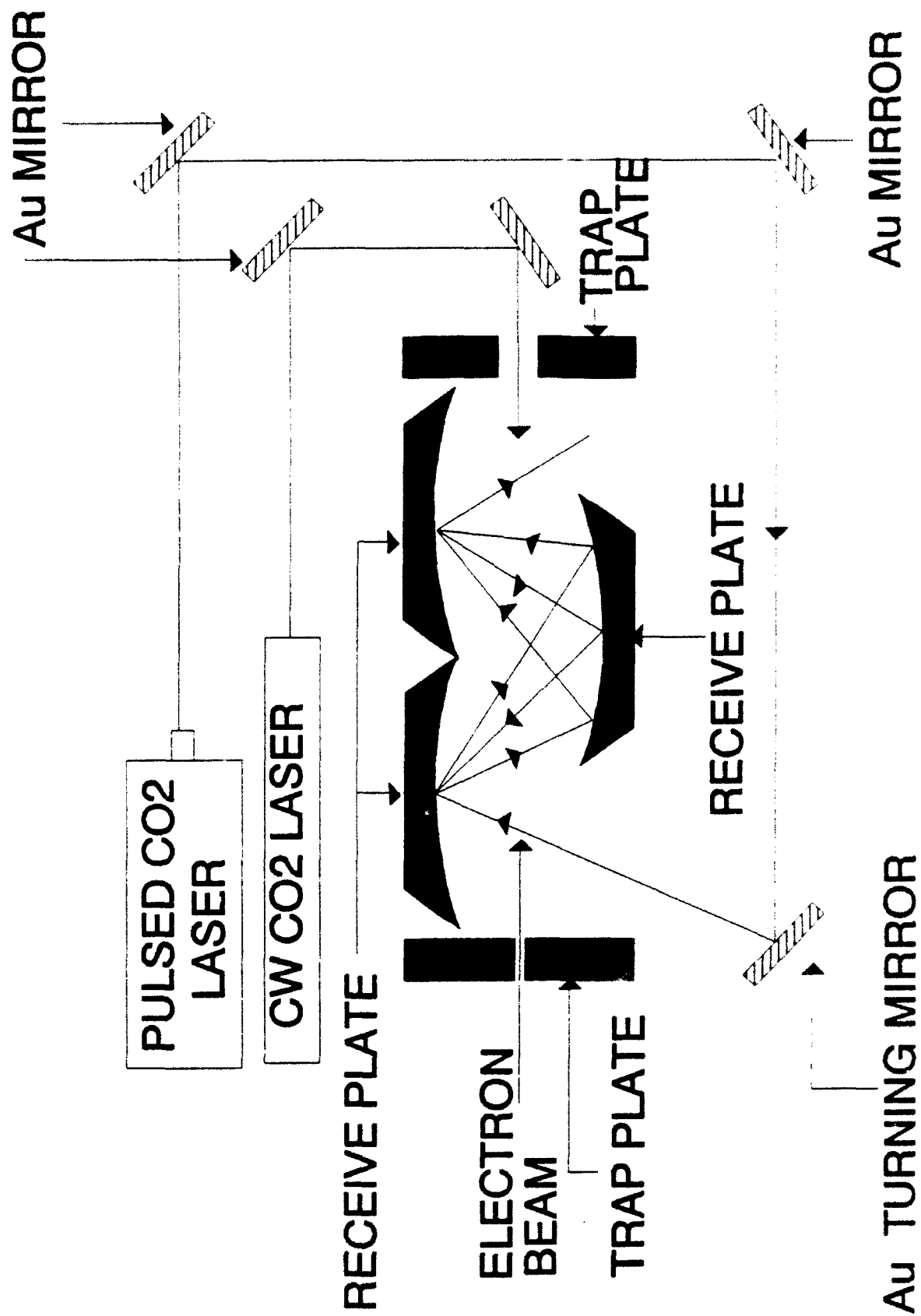
Figure 1. Schematic representation of the modified White-type cell and the two laser beam pathways.

Figure 2. Experimental pulse sequence employed in the two-laser probe-pump technique. The ejections after the probe laser and the pump laser gating steps were eliminated when only one-laser experiments were performed.

Figure 3. One-laser infrared multiple photon dissociation spectra of (a) protonated molecular ion of diglyme, (b) positive molecular ion of 3-bromopropene, and (c) negative molecular ion of $\text{Ga}(\text{hfac})_3$ at a probe laser energy of 1 J pulse^{-1} . Error estimates are 95% confidence limits.

Figure 4. Two-laser infrared multiple photon dissociation spectra of (a) protonated molecular ion of diglyme, (b) positive molecular ion of 3-bromopropene, and (c) negative molecular ion of $\text{Ga}(\text{hfac})_3$ at a probe laser energy of $100 \text{ mJ pulse}^{-1}$ and a pump laser energy of 1 J delivered in a 30 ms pulse. Error estimates are 95% confidence limits.

Figure 5. Gas phase neutral infrared spectra of (a) diglyme, (b) 3-bromopropene, and (c) $\text{Ga}(\text{hfac})_3$.



Time

